THERMAL ANALYSIS STUDIES ON KARYA MAGNESITE FROM KARNATAKA

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Magnesite mineral from Karya deposit in Karnataka is found associated with impurities, mainly, dolomite, calcite, quartz and hornblende which are highly noxious for the refractory properties of this mineral. Thus, this poor grade mineral needs beneficiation before it can be used in the ceramic industry for refractory purposes.

In the present paper, the Karya magnesite has been studied by thermal analyses i.e. Differential thermal analysis (DTA) and Thermogravimetric analysis (TGA). The mineral has been beneficiated by physical methods viz., sink and float and size reduction and three different grades' samples have been obtained from the raw sample. Thermal analysis techniques have been used to assess the quality of each grade and the quality difference in them.

The amount of the carbonate minerals has been estimated qualitatively by DTA and quantitatively by TGA. It has been found that the sample A contains least amount of impurities and thus it is a better quality material whereas sample C is of very poor quality containing maximum amount of impurities. On fractionation of sample C, the results have shown that the finer fraction contains less impurities than the coarser one.

It may be said that this mineral can be easily beneficiated to a great extent by the methods used here.

INTRODUCTION

Demand for high quality bricks is escalating geared by the advancement in technology of metal extraction especially in iron and steel-making. The steel-making technology is rapidly changing to attain high quality that the acidic bricks used earlier are replaced by basic bricks i.e. magnesia bricks. The specifications for bricks are becoming stringent with time. Much work has already been done on production of high quality magnesia from sea-water to meet the demands of the industry but still the natural magnesite is preferred for making bricks as the sea-water magnesia is expensive as well as it contains fluxing material such as boria.1 Natural magnesite is found associated with impurities mainly, dolomite, calcite and quartz. These impurities damage the refractoriness of this mineral. The quality of natural magnesite being mined is depleting with time. Thus it is quite clear that an effort is needed in the area of beneficiation of poor quality magnesite.2

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Before beneficiation of the mineral, it is a must to know the nature of the impurities present in it and also to know the nature of the association between wanted material and the impurities. After beneficiation, characterisation is necessary to know the quality of the beneficiated product and the extent of its beneficiation from the raw material. Thermal analysis techniques i.e. Differential Thermal Analysis (DTA) and Thermogravimetric Analysis (TGA) are very useful to characterise carbonate minerals, like magnesite, calcite and dolomite which undergo decomposition reactions with absorption of energy evolving out carbon dioxide. These endothermic effects are so much characteristic, well defined and of high magnitude that even very small amount of these minerals can be easily detected by DTA as shown by Webb and Krüger. Differentiation between dolomite and the mixture of calcite and magnesite can also be done by DTA. Quantitative analysis of these minerals can be done by none other than TGA.

Magnesite from Karya deposit in Karnataka has been characterised by XRD, IR, DTA, TGA and ignition loss measurements by Khandal et al. and results have been reported elsewhere. This mineral is of poor grade containing mainly calcite, dolomite and quartz. The present study deals with the thermal analysis of this mineral divided into different grades. The raw mineral has been divided into three grades by physical methods of beneficiation. Thermal analysis of all these three samples have been done to see whether the beneficiation has taken place or not and also to assess the extent of beneficiation.

Materials and Methods

Sample Preparation

The sample collected from the field was subjected to crushing and grinding. A representative sample around 1kg was obtained from 50kg of original sample following coning and quartering technique. This sample was then subjected to physical methods of beneficiation i.e. sink and float using bromoform and three products were obtained as shown in flow diagram (chart 1). These three samples have been described here as sample A, B and C. Sample C was further subjected to fractionation and two fractions i.e. coarser and finer were obtained. Analyses have been done on all these five samples.

Chemical Analysis

The raw sample and its three separated samples were analysed by conventional method given by IS specification for ceramic materials. The results showing different constituents of the samples are shown in Table I.

Thermal Analysis

All the samples were analysed by DTA and TGA on NETZSCH thermal analyser upto 1000 °C at the heating rate of 10 °C/minute. α-Al2O3 was used as a reference material. Both DTA and TGA were recorded simultaneously. In each case 150mg of the sample was taken for the studies. The results are shown in Fig. 1 (DTA) and Fig. 2 (TGA).
SAMPLE A = (S₁ + S₂)
SAMPLE B = FLOAT (5mm, -30mm)
SAMPLE C = FLOAT (-10mm)

CHART 1 Flow diagram for different samples.

TABLE 1

Chemical analysis of the samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>MgO (%)</th>
<th>CaO (%)</th>
<th>SiO₂ (%)</th>
<th>Mixed Oxides (%)</th>
<th>L. O. I.</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>42.74</td>
<td>0.28</td>
<td>5.72</td>
<td>2.30</td>
<td>48.58</td>
<td>99.62</td>
</tr>
<tr>
<td>B</td>
<td>41.32</td>
<td>3.64</td>
<td>4.26</td>
<td>1.60</td>
<td>48.15</td>
<td>98.97</td>
</tr>
<tr>
<td>C</td>
<td>39.31</td>
<td>5.04</td>
<td>6.20</td>
<td>2.50</td>
<td>46.15</td>
<td>99.20</td>
</tr>
<tr>
<td>C (coarser)</td>
<td>36.00</td>
<td>3.33</td>
<td>8.50</td>
<td>5.40</td>
<td>46.65</td>
<td>99.88</td>
</tr>
<tr>
<td>C (finer)</td>
<td>38.08</td>
<td>5.04</td>
<td>4.40</td>
<td>5.60</td>
<td>44.67</td>
<td>97.79</td>
</tr>
</tbody>
</table>

RESULTS AND DISCUSSION

Chemical Analysis

The results of chemical analysis (Table I) indicate that the original sample when divided into three grades exhibited change in the content of MgO. Original sample contains very low amount of MgO but sample A shows very high amount of MgO. Chemical analyses of sample A, B and C indicate that the original sample
can be beneficiated easily by physical methods as there is a rise in the MgO content in sample A and at the same time there is a decrease in the content of CaO and SiO₂ in other samples. This much difference is sufficient to take advantage in order to enrich the MgO content of the raw sample. Sample C, on fractionation show significant liberation, coarser fraction having more silica than the finer fraction.

Differential Thermal Analysis (DTA)

The DTA curves are shown in Fig. 1. It may be seen from here that all the five samples show three endothermic changes. The first one at around 670 °C is the most intense and sharp peak in all the cases. The other two peaks at around 750 °C and 880 °C are very small peaks. Out of these latter two peaks the one at 880 °C is bigger in size. The same nature of the thermograms indicate the presence of same mineral in all these samples. The only difference which can be clearly noticed is that the sizes of these peaks are different for different samples. The

Fig 1 Differential thermal analysis of samples.
difference in size of the peaks-peaks of the different amount of the mineral present there in.

The first intense peak represents the decomposition of magnesite evolving out Carbon dioxide. The big size of this peak indicates that in all the five samples main mineral is magnesite. The second peak at around 750 °C represents the decomposition of magnesite part of dolomite. The difference in the temperature of decomposition of magnesite pure and magnesite forming dolomite is well-known and it is because of the fact that some extra energy is required to break the structure of 1:1 compound before decomposition of its magnesite part. It is for this reason that the decomposition is observed at a little higher temperature for dolomite. The small size of this peak shows that the dolomite content is very small in comparison to the magnesite content as the size of the peak representing magnesite is very large. The third peak around 880 °C represents the evolution of carbon dioxide from calcite. This calcite can be present in the sample either as free calcite or and calcite in dolomite as there is no difference in decomposition temperature of two types of calcite. One can have an idea from the size of the peaks whether free calcite is there or not. The bigger size (significantly) of this peak at 880 °C than that of the peak at 750 °C predicts the presence of free calcite in the sample. It has already been shown by Webb that pure dolomite on DTA should have the following relation. as far as the sizes of the two peaks are concerned.

\[ 1.53 = \frac{\text{Size of the second peak (880 °C)}}{\text{Size of the first peak (750 °C)}} \]

If the ratio is more than the value shown above, it clearly indicates that the sample contains free calcite also along with dolomite.

In the present study areas of all the peaks for different samples were calculated and are shown in Table II. It may be seen that the ratio of second peak to first peak is more than 1.53 in all the cases, which means that the calcite is present in all the samples along with dolomite. It may also be seen that amount of calcite and dolomite is minimum in Sample A as the areas of the peaks representing these

<table>
<thead>
<tr>
<th>Sample</th>
<th>Size of the peaks cm²</th>
<th>Ratio = Peak at 880 °C/Peak at 750 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Peak at 670 °C</td>
<td>Peak at 750 °C</td>
</tr>
<tr>
<td>A</td>
<td>20.5</td>
<td>0.05</td>
</tr>
<tr>
<td>B</td>
<td>18.25</td>
<td>0.25</td>
</tr>
<tr>
<td>C</td>
<td>16.5</td>
<td>0.65</td>
</tr>
<tr>
<td>C (coarser)</td>
<td>17.75</td>
<td>0.40</td>
</tr>
<tr>
<td>C (finer)</td>
<td>18.00</td>
<td>0.50</td>
</tr>
</tbody>
</table>
minerals are minimum in this case. Sample C has maximum amount of calcite whereas sample B and Sample C (coarser) have maximum amount of dolomite. This clearly indicates that Karya Magnesite can be easily broken down into good and bad quality materials by just physical methods. Sample C, when fractionated also exhibited the change in amount of the minerals. The finer fraction shows different analysis in comparison to the coarser one. Thus, liberation is taking place in this mineral quite significantly.

It may be mentioned here that all the samples exhibit a small exothermic effect at around 830°C. This peak is a normal feature of carbonate minerals, especially, of magnesium and calcium and one may not be confused by this taking it as for something else. This has been well studied in the past by many workers. According to Kulp et al., this peak is attributed to the differences in the thermal properties (thermal diffusivity) of carbonates and the resulting oxides. The mineral sample attains a transiently high thermal diffusivity at that temperature.

**Thermogravimetric Analysis (TGA)**

Thermograms of all the five samples are shown in Fig. 2. The curves are showing loss in weight with the temperature. The first loss in weight in the region of

![Fig 2](image)

**Fig 2** Thermogravimetric analysis of samples.
600–700 °C is maximum among losses in three temperature regions observed here. The second loss in weight is seen in the region of 725–800 °C and third one in the region of 840–940 °C. All the samples showed similar type of curves. Each loss in weight here corresponds to the endothermic effect observed in DTA (Fig. 1). Maximum loss in weight in the region of 600–700 °C represents the evolution of carbon dioxide from magnesite mineral. It is easy to calculate the amount of the magnesite mineral in the sample from this loss in weight (Table III). The second and third weight losses are due to carbon dioxide coming out of the magnesite and calcite part of dolomite and free calcite. All these changes can be shown in the following manner as described by Canterford et al. 12

<table>
<thead>
<tr>
<th>Sample</th>
<th>Magnesite (%)</th>
<th>Calcite (%)</th>
<th>Dolomite (%)</th>
<th>Total (%)</th>
<th>Others (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>92.94</td>
<td>0.76</td>
<td>2.09</td>
<td>95.76</td>
<td>4.24</td>
</tr>
<tr>
<td>B</td>
<td>86.38</td>
<td>1.52</td>
<td>9.74</td>
<td>97.84</td>
<td>2.16</td>
</tr>
<tr>
<td>C</td>
<td>77.66</td>
<td>3.04</td>
<td>5.60</td>
<td>86.30</td>
<td>13.70</td>
</tr>
<tr>
<td>C (coarser)</td>
<td>76.40</td>
<td>1.52</td>
<td>12.54</td>
<td>90.46</td>
<td>9.54</td>
</tr>
<tr>
<td>C (finer)</td>
<td>80.22</td>
<td>3.04</td>
<td>6.89</td>
<td>90.15</td>
<td>9.85</td>
</tr>
</tbody>
</table>

1. Wt. loss in the region of 600–700 °C
   Magnesite + Calcite + Dolomite → MgO + CO₂

2. Wt. loss in the region of 725–800 °C
   Dolomite + Calcite → MgO + Calcite + CO₂

3. Wt. loss in the region of 850–940 °C
   Calcite → CaO + CO₂

Assuming that the dolomite present in the samples has a 1:1 ratio of magnesite and calcite the amount of dolomite and calcite can be calculated from the losses in weight for all the samples corresponding to these minerals. It may be seen from Table III that the amount of dolomite, calcite and magnesite are different for all the samples which complements the DTA studies. It may be said that the separation of impurities from the magnesite can be brought about by physical methods as there occurs a change in the amount of different minerals even on fractionation.

**CONCLUSION**

Thermal analysis techniques give a clear picture of the constitution of magnesite mineral. The analyses can be used to find out the amount of calcite and dolomite (chief impurities of magnesite) in a sample. This way, characterisation of beneficiated product becomes easier.
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